Ferroelectric Properties of a Fast Switching Cyclic Siloxane Oligomer

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The synthesis and properties of a novel ferroelectric cyclic siloxane oligomer are reported. The properties of the oligomer are compared to those of a linear siloxane polymer and its unattached side group consisting of the same mesogenic moiety as the cyclic siloxane oligomer. The ferroelectric and electroclinic response times as well as the tilt angles of the cyclic material are found to be similar to those of the monomer while the spontaneous polarization is comparable to that of the linear siloxane polymer. These studies constitute the first detailed comparison of the ferroelectric properties of cyclic and linear siloxane polymers.

Introduction

Low molar mass ferroelectric liquid crystals (FLC) with high lateral dipole moments are known to exhibit fast response times. Such molecules show properties such as large polarization and low viscosity, needed for display applications, but lack the wide range of thermal stability of the ferroelectric phase and mechanical stability. One approach to overcome these problems was the development of FLC polymers.[1−3]

It has been observed that the attachment of the FLC side group to a flexible backbone such as polysiloxane leads to an enhancement of the smectic C* phase but is often accompanied by a decrease in the spontaneous polarization (P_S), an increase in viscosity, and therefore a slower switching process. Moreover, there are device fabricating difficulties including capillary filling in the isotropic phase due to the high viscosity. A new approach to design fast switching FLCs is to include a cyclic siloxane (instead of a linear siloxane) as the backbone into the molecular structure.

The first examples of cyclic siloxanes with liquid-crystalline properties were presented in 1981.[4] Although there has been a great deal of activity in developing cyclic oligosiloxanes since then, most of these studies are on materials exhibiting nematic or cholesteric liquid-crystalline phases.[5−18] There exist only three examples of cyclic siloxane smectic C* materials,[19−21] and even in these cases a detailed study of

the ferroelectric properties has not appeared to have been carried out.

In this paper we present the synthesis of a new mesogenic cyclic siloxane with fast electroclinic and ferroelectric switching in the smectic A phase and the smectic C* phase, respectively. Its phase behavior, spontaneous polarization, optical tilt angle, and electrooptic properties are compared with those of the unattached side group and a linear polysiloxane with the same mesogenic moiety.

Experimental Section

Techniques. Analytical TLC was conducted on Whatman precoated silica gel 60-F254 plates. The 300 MHz ^{1}H NMR spectra were recorded on a Bruker MSL300 spectrometer. All spectra were run in CDCl$_3$ or DMSO solutions. Infrared spectra were obtained by using a FT Perkin-Elmer 1800 spectrometer and KBr pellets. GC-MS chromatograms were recorded on a Finnegan ion-trap mass spectrometer connected to a Hewlett-Packard 5890 GC (50 cm × 0.2 mm column, OV-101). The phase identification was performed by optical texture observations using a Nikon polarizing microscope equipped with a Mettler hot stage. The phase transition temperatures were determined by using a Perkin-Elmer DSC-7 differential scanning calorimeter (scan rate 10 K/min). The spontaneous polarization (P_S) was measured by the triangular wave method.[22] A 30 V amplitude triangular wave (frequency range 0.1−100 Hz) was applied across a commercially avail-

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able 5 μm thick Linkam cell. The current was determined by measuring the voltage drop across a reference resistance with a storage oscilloscope. The polarization current was separated from the ohmic and capacitive contributions and then integrated by a computer. The electrooptic switching times (τ) were determined using a photodiode measuring the transmitted light of the sample placed between crossed polarizers. The switching time is defined as the time required for an intensity change from 10% to 90% on applying a square wave. A 40 V amplitude square wave (frequency 10 Hz) was applied to the cells for the experiments. The tilt angles (θ) were measured manually applying a 40 V amplitude square wave (frequency 1 Hz) between crossed polarizers using a rotatable microscope table.

Materials. Gel permeation chromatography was performed on Bio-Beads SX1 gel obtained from Bio-Rad. The initial poly-(hydrogenomethylsiloxane) ($M_n = 2270$) was purchased from Petrach Systems, Inc., and the pentacyclohydrogenomethylsiloxane from United Chemical Technologies, Inc., and used as received. The average number molecular weights of the initial polysiloxane has been determined by osmometry, and the obtained values were in agreement with the values given by the commercial source.

Synthesis. *4′-(9-Decenyloxy)biphenyl-4-carboxylic Acid Methyl Ester (3).* To a nitrogen-flushed flask, kept at 0 °C, and 960 mg (40 mmol) of oil-free sodium hydride was added 150 mL of dry DMF. 4′-Hydroxybiphenyl-4-carboxylic acid methyl ester (**1**, (11.84 g, 30 mmol) in 40 mL of DMF was added, and the mixture was stirred for 30 min. A solution of 6.57 g (30 mmol) of 10-bromo-1-decene (**2**) in 20 mL of DMF was added dropwise to the suspension. The resulting mixture was allowed to stir for 1 h at room temperature and 8 h at 80 °C. The solvent was removed by rotary evaporation in vacuum and excess sodium hydride was quenched by addition of water. HCl solution (1 N) was poured into the mixture and the resulting precipitate was filtered and washed with 10% aqueous sodium bicarbonate solution and water. The crude product was recrystallized twice from ethanol to yield 8.7 g (79%) of **3**. R_f 0.8 (dichloromethane); ^{1}H NMR (CDCl$_3$, TMS) δ (ppm) 1/2−2.08 (m, 14 H, (CH$_2$)), 3.98 (t, 2H, C*H$_2$*−O), 4.02 (s, 3H, O−C*H$_3$*), 5.02 (m, 2H, CH=C*H$_2$*), 5.80 (m, 1H, C*H*=CH$_2$), 6.95−8.1 (m, 8H, ArH). Anal. Calcd for C$_{24}$H$_{30}$O$_3$: C, 78.68; H, 8.19. Found: C, 78.54; H, 8.08.

Hydrolysis. *4′-(9-Decenyloxy)biphenyl-4-carboxylic Acid (4)* was obtained by a hydrolysis of the ester derivative **3** in the presence of KOH/ethanol. The crude product was recrystallized from acetic acid to yield 90% of **4**. R_f 0.5 (ethyl acetate); ^{1}H NMR (DMSO, TMS) δ (ppm) 1.18−2.1 (m, 14H, (CH$_2$)), 3.96 (t, 2H, C*H$_2$*O), 5.02 (m, 2H, CH=C*H$_2$*), 5.75 (m, 1H, C*H*=CH$_2$), 6.98−8.15, (m, 8H, ArH). Anal. Calcd for C$_{23}$H$_{28}$O$_3$: C, 78.40; H, 7.95. Found: C, 78.80; H, 7.75.

1-(Benzyloxy)-4-[(R)-(+)-(1-carboethoxy)ethoxy]benzene (7). To 4.48 g (38 mmol) of ethyl-(*S*)-(−)-lactate (**6**), 10 g (50 mmol) of 4-(benzyloxy)-phenol (**5**) and 13.1 g (50 mmol) of triphenylphosphine (TPP) was added 200 mL of dichloromethane. To this mixture was added dropwise a solution of 20 mL of dichloromethane and 8.14 mL (50 mmol) of diethylazodicarboxylate (DEAD). The reaction mixture was stirred overnight at room temperature. After evaporation of the solvent, the residue was subjected to column chromatography on silica gel with 1/4 ethyl acetate/hexane as eluting solvent to yield 7 g (61%) of product **7** (mp 52 °C): R_f 0.5 (1/4 ethyl acetate/hexane); ^{1}H NMR (CDCl$_3$, TMS) δ (ppm): 1.2 (t, 3H, CH$_2$−C*H$_3$*), 1.63 (d, 3H, CH−C*H3*), 4.2 (q, 2H, C*H$_2$*−CH$_3$), 4.82, (q, 1H, C*H*−CH$_3$), 5.01 (s, 2H, Ar−C*H$_2$*−O), 6.88 (s, 4H, O−Ar−O), 7.3−7.75 (m, 5H, Ar−C*H$_2$*). Anal. Calcd for C$_{18}$H$_{20}$O$_4$: C, 72.00; H, 6.66. Found: C, 71.90; H, 6.72.

p-[(R)-(+)-1-(Ethoxycarbonyl)-1-ethoxy]phenol (8). Hydrogen was allowed to bubble through a stirred suspension of 10% palladium on carbon (0.4 g) in 40 mL of dichloromethane. After 15 min 7 g (23 mmol) of the benzyl ether **7** was added, and the reaction mixture stirred overnight. The reaction was monitored by TLC (1/4 ethyl acetate/hexane). The suspension was filtered through a Celite pad. The solvent was removed by rotary evaporation, and the crude product was distilled under vacuum (0.01 Torr/130 °C) to yield 4.5 g (91%) of **8**. R_f

0.2 (1.4 ethyl acetate/hexane); ^{1}H-NMR (CDCl$_3$, TMS) δ (ppm): 1.2 (t, 3H, CH$_2$-C*H$_3$*), 1.63 (d, 3H, CH-C*H$_3$*), 4.2 (q, 2H, C*H$_2$*-CH$_3$), 4.8, (q, 1H, C*H*-CH$_3$), 6.3 (broad s, 1H, OH), 6.75 (s, 4H, ArH). Anal. Calcd for C$_{11}$H$_{14}$O$_4$: C, 62.85; H, 6.66. Found: C, 62.90; H, 6.55.

(R)-(+)-4′-(1-(Carboethoxy)ethoxy)phenyl-4-[4-(9-decenyloxy)-phenyl] Benzoate (10PPB2). A mixture of **4** (2.11 g, 6 mmol), thionyl chloride (20 mL), and two drops of DMF was refluxed for 3 h at 80 °C. The remaining thionyl chloride was removed under vacuum. To the mixture of the acid chloride **4b** and the phenol derivative **8** (1:1 mole ratio) were added 1 mL of pyridine and a few crystals of 4-(dimethylamino)pyridine (DMAP) in 30 mL of dichloromethane under nitrogen. After 3 days of stirring at room temperature, the mixture was quenched with 10% HCl (aqueous), washed with 5% sodium hydroxide solution and brine, and then dried over MgSO$_4$. After the removal of the solvent the crude product was purified by column chromatography on silica gel (1/4 ethyl acetate/hexane). The product was recrystallized from ethanol to yield 1.8 g (55%) of **10PPB2** (Chart 1). The purity of the product was greater than 99% as ascertained by GC. R_f 0.5 (1/4 ethyl acetate/hexane); ^{1}H NMR (CDCl$_3$, TMS) δ (ppm) 1.2 to 2.08 (m, 20H), 3.98 (t, 2H, −C*H$_2$*−O), 4.2 (q, 2H, O−C*H$_2$*−CH$_3$), 4.8 (q, 1H, O−C*H*−), 4.9 (m, 2H, C*H$_2$*=CH−), 5.82 (m, 1H, C*H*=CH$_2$), 6.95 to 8.2 (m, 12H, arH). Anal. Calcd for C$_{34}$H$_{40}$O$_6$: C, 75.00; H, 7.35. Found: C, 74.85; H, 7.25.

Synthesis of the Ferroelectric Polymers. To a solution of poly(hydrogenomethylsiloxane) ($M_n = 2270$), 0.36 mmol of SiH function (or pentacyclohydrogenomethylsiloxane respectively) dissolved in 50 mL of dry toluene was added 218 mg (0.4 mmol) of **10PPB2**. The reaction mixture was heated to 70 °C under nitrogen. A solution of 40 μL of the dicyclopentadienylplatinium(II) chloride catalyst in dichloromethane (1 mg of catalyst/mL of dichloromethane). The mixture was refluxed under nitrogen for 3 days. The polymer was purified by gel permeation chromatography eluting with toluene. The fractions containing the polymer were gathered, and the polymer was isolated by precipitation from a THF solution into methanol. The pure polymer (cyclic siloxane respectively) was obtained in 60% yield and dried under vacuum at 60 °C. The disappearance of the ^{1}H NMR peak of each of the polymers corresponding to the SiH groups ($\delta = 4.74$ ppm, CDCl$_3$) and the ratios of the integrated areas of the various proton environments confirmed that virtually all of the Si−H bonds had been converted to Si−mesogenic group bonds.

Results and Discussion

Synthesis of the Materials. Scheme 1 shows the reaction pathway for the mesogenic side group **10PPB2**. 4′-Hydroxybiphenyl-4-carboxylic acid methyl ester (**1**)[23] reacted with 10-bromo-1-decene (**2**) in the presence of NaH, followed by hydrolysis to give 4′-(9-decenyloxy)-biphenyl-4-carboxylic acid (**4**). The etherification of 4-(benzyloxy)phenol (**5**) with ethyl (*S*)-(−)-lactate (**6**) via the Mitsunobu reaction[24] in the presence of triphenylphosphine (TPP) and diethylazodicarboxylate (DEAD) gave product **7**. The Mitsunobu reaction proceeds with an inversion of the configuration at the chiral center. The hydrogenolytical deprotection of its hydroxy function led to the phenol derivative **8**. The mesogen **10PPB2** was obtained by the reaction of the acid chloride of **4** with **8** in the presence of pyridine. The corresponding polysiloxane **10PPB2-P** and the cyclic siloxane **NJI** (Scheme 2) were obtained through the classical hydrosilylation reaction between the vinyl mesogenic group **10PPB2** and poly(hydrogenomethylsiloxane) ($M_n = 2270$) or pentacyclohydrogenomethylsiloxane in the presence of a platinum catalyst. The

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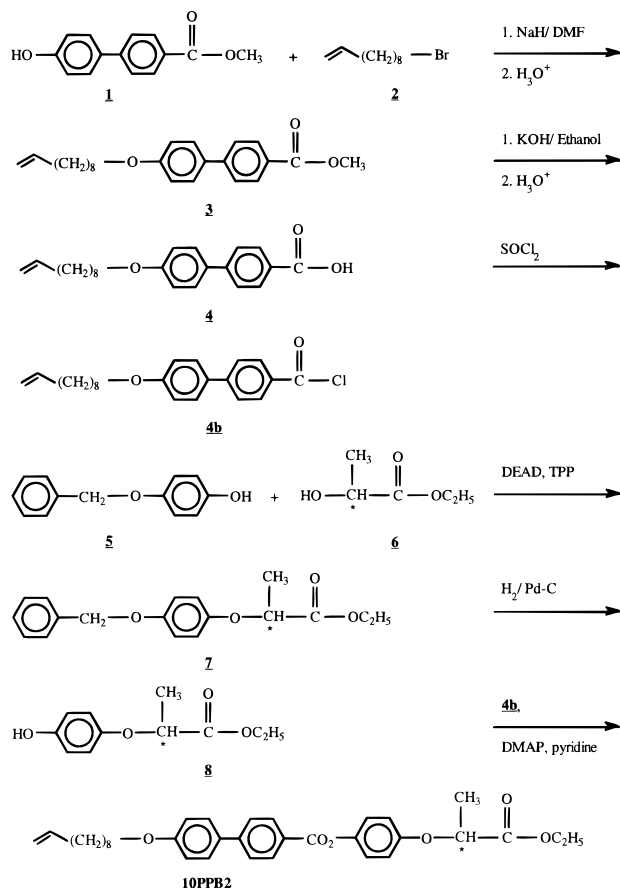**Scheme 1. Reaction Pathway for the Mesogen 10PPB2**

Figure 1. Temperature dependence of the spontaneous polarization of **10PPB2**, **NJI**, and **10PPB2-P**.

Figure 2. Temperature dependence of the optical tilt angle of **10PPB2**, **NJI**, and **10PPB2-P**.

Scheme 2. Reaction Pathway for the Linear Polysiloxane 10PPB2-P and the Cyclic Siloxane NJI

Table 1. Phase Sequence and Phase Transition Temperatures

material	phase sequence (°C)
10PPB2	S_I or S_F 53.9 S_C* 93.9 S_A 123.9 I
NJI	K 68 S_C* 167.8 S_A 185.2 I
10PPB2-P	g 25 X 58 S_C* 178 S_A 215−222 I

products were purified by gel permeation chromatography and precipitated from THF solution into methanol.

Phase Transition Temperatures. The phase sequence of the materials is given in Table 1. These data were obtained by a combination of polarization microscopy and differential scanning calorimetry (DSC). We observe an enhancement of the thermal range of the mesophases on polymerization, an effect reported earlier for many side-chain polymeric systems[25−27] with a linear polysiloxane backbone. The smectic C* (S_C*) phase ranges of the siloxanes **NJI** (temperature range $\Delta T \approx$ 100 K) and **10PPB2-P** ($\Delta T \approx$ 120 K) are dramatically broader compared to the range of the monomer **10PPB2** ($\Delta T \approx$ 40 K). In case of the smetic A (S_A) phase we only see a small enhancement for the range of the polysiloxane ($\Delta T \approx$ 40 K) compared to that of the monomer ($\Delta T \approx$ 30 K), while the cyclic siloxane **NJI** shows a much smaller range ($\Delta T \approx$ 18 K). As expected, the polymerization increases the phase transition temperatures.

Electrooptical Studies. We have investigated the behavior of the liquid-crystal materials in an electrical field. The experiments were performed in commercially available 5 μm Linkam cells. We have measured the spontaneous polarization (Figure 1) and the optical tilt angle (Figure 2) in the S_C* phase as well as the electrooptical switching time (Figures 3−7) in the S_C* and the S_A phase of the three compounds.

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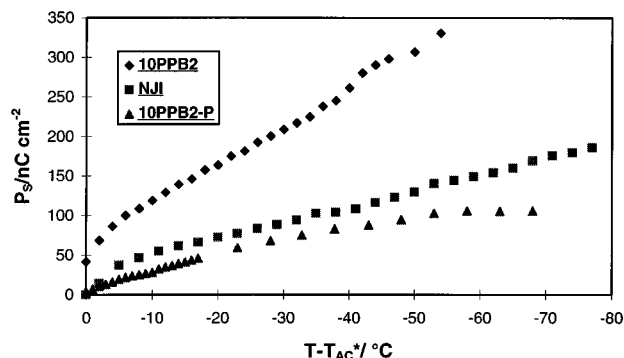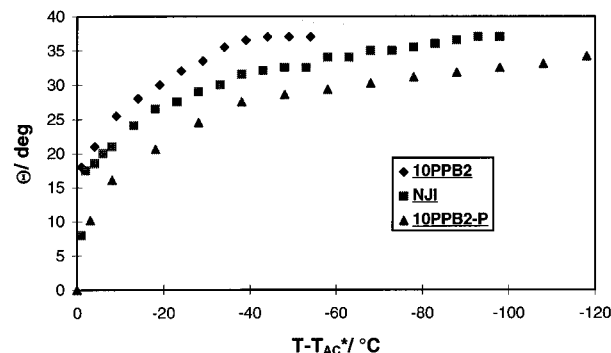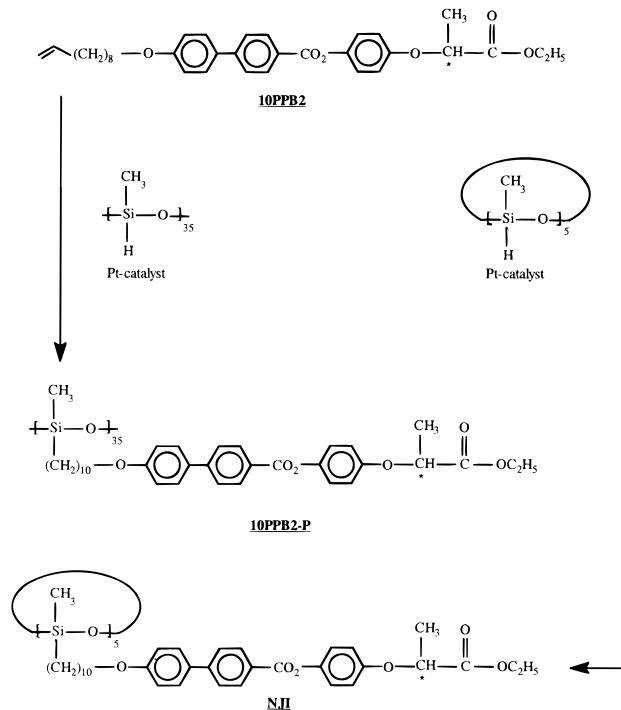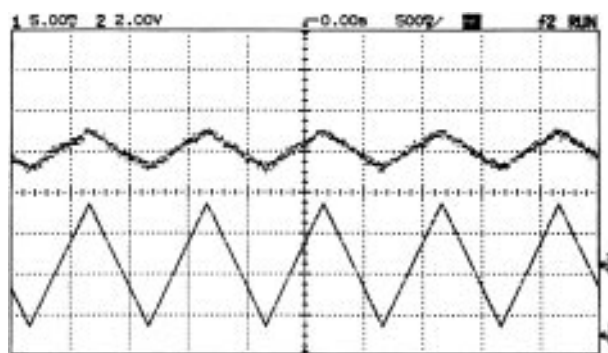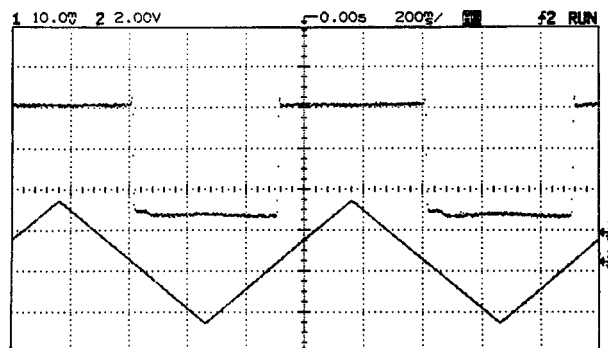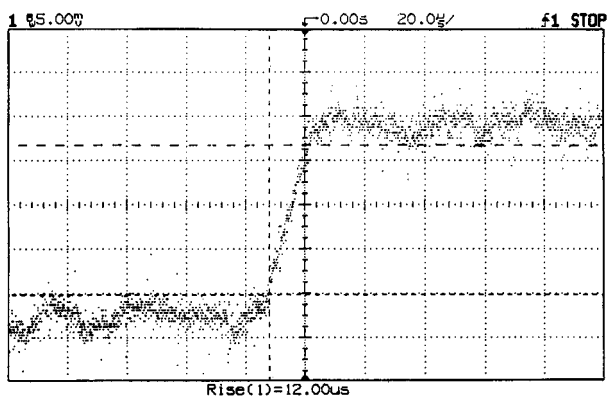
Figure 3. Optical response of **NJI** to an applied triangular wave at 180 °C in the smectic A phase.
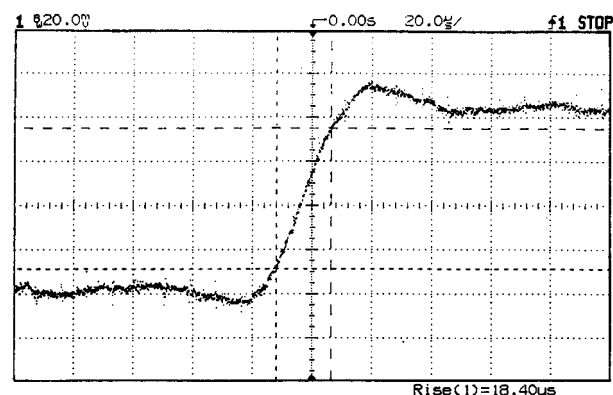

Figure 4. Optical response of **NJI** to an applied triangular wave at 160 °C in the smectic C* phase.
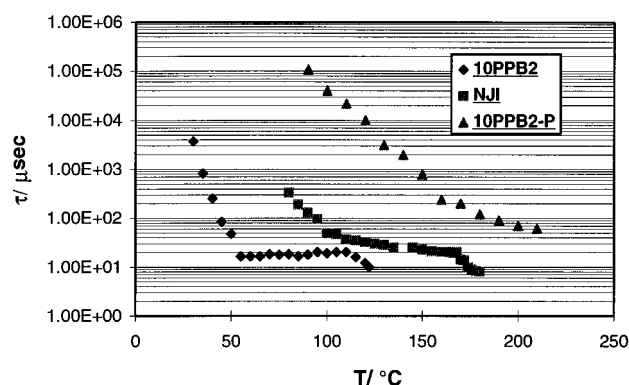

Figure 5. Optical transmission on applying a 40 V amplitude square wave (frequency 10 Hz) to **NJI** at 180 °C in the smectic A phase.

Figure 6. Optical transmission on applying a 40 V amplitude square wave (frequency 10 Hz) to **NJI** at 160 °C in the smectic C* phase.

Figure 7. Temperature dependence of the switching time in the smectic A and the smectic C* phase of **10PPB2**, **NJI**, and **10PPB2-P**.

The temperature dependence of the **spontaneous polarization** (P_S) is given in Figure 1. The monomer **10PPB2** exhibits the highest spontaneous polarization among the three ferroelectric liquid crystals—a value of 262 nC/cm² (at $T - T_{AC}^* = -40$ °C). By attaching a siloxane backbone, we find a 55% decrease in P_S for **NJI** and 65% for **10PPB2-P** at the same reduced temperature. Such a decrease in P_S on polymerization has been observed before[26] and is attributable to the increased dilution of the dipoles in the polymer.[28] In the higher ordered smectic phase of **10PPB2** we observe ferroelectric behavior and P_S increases up to 330 nC/cm² at ($T - T_{AC}^*$) = -54 °C.

The **optical tilt angle** θ increases with the decrease of temperature in the S_C^* phase (Figure 2). Although

the saturation value of the tilt angle is similar for the three materials (in the range 34−37°), the θ value of NJI (compared at any reduced temperature in the S_C^* phase) is intermediate between those of the monomer and the linear polymer. This indicates that the molecular packing of the mesogenic moiety is different in all the cases and is affected by the coupling of the side group to the siloxane backbone.

Figure 3 shows the **optical response** of **NJI** in the S_A phase upon application of a triangular wave. The optical response follows the applied voltage confirming the soft-mode behavior associated with the electroclinic effect.[29,30] Figure 4 illustrates the classical ferroelectric response to an applied triangular wave in the smectic C* phase of the cyclic siloxane.

The oscilloscope traces of the optical transmistion on applying a square-wave voltage to **NJI** in the S_A and S_C^* are given in Figures 5 and 6, respectively. Clearly, the response time is extremely fast in both phases. We measured a rise time of 12 μs in the S_A phase at 180 °C (Figure 5) and 19 μs in the S_C^* phase at 160 °C (Figure 6).

The temperature dependence of the **electrooptical response times** (τ) associated with the ferroelectric and electroclinic modes of the three materials are given in Figure 7. The switching times of the cyclic siloxane **NJI** and the unattached monomer **10PPB2** are in the same order of magnitude in the S_A and S_C^* phases. In comparison, the response times of the linear polymer

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are much slower. This is a surprising result, particularly since the spontaneous polarization of **NJI** is much lower than the P_S of the monomer. It is an indication of an increased cooperative motion of the mesogenic groups in the cyclic siloxane oligomer. It also indicates that the cyclic backbone does not affect the Goldstone or soft-mode dynamics of the mesogen. This could conceivably be due to the structure of the cyclic siloxane oligomer. The cyclic backbone is relatively small (five siloxane units) and does not affect the cooperative motion of the mesogens which are practically decoupled from the backbone due to the long flexible spacer. In contrast, in the case of the linear polymer the backbone consists of 35 siloxane units slowing down the switching dynamics drastically. Detailed X-ray studies on the structure of **NJI** have been published elsewhere.[31]

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Conclusion

We have shown that it is possible to preserve the electrooptical properties of the monomer-like fast electroclinic/ferroelectric switching as well as the high optical tilt angle in the cyclic siloxane oligomer. At the same time an enhancement of the temperature range of the smectic C* phase was observed. These properties are interesting from the point of view of application. The dependence of these properties on the number of siloxane units in the cyclic ring system would be of interest.

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